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The Action of Acid Chlorides upon Trimethylamine. The Action of Hydroxylamine upon Sulfinic Acids and their Derivatives

A DISSERTATION

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THE ACTION OF ACID CHLORIDES UPON TRIMETHYLAMINE

Several years ago, Vorländer and Nolte[1] announced a singular quaternary ammonium salt in which a so-called "negative" radical, benzenesulfonyl, assumed the role ordinarily played by an alkyl group. They claimed that benzenesulfonyl chloride acted upon a water solution of trimethylamine to replace the "imino" hydrogen atom of the ammonium base as follows.

$$(CH_3)_3\equiv N(OH)-H + C_6H_5SO_2Cl = (CH_3)_3\equiv N(Cl)-SO_2C_6H_5 + H_2O \qquad (1)$$

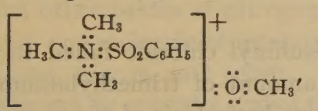
In their opinion, the presence of this salt was established by the formation of a chloroplatinate[2] which could be decomposed by hydrogen sulfide to restore the original chloride. A solution of this chloride in water was neutral in reaction to indicators. These facts led them to conclude that the salt-like nature of ammonium compounds depends but little upon the "positive" or "negative" character of the radicals associated with nitrogen in the ammonium complex.

The usual properties ascribed to this salt suggested that it would be serviceable in the preparation of electromers similar to those described by Jones.[3,4] We proposed, first, to allow sodium methylate to act upon this chloride and, second, to treat trimethylmethoxyl-ammonium iodide, $(CH_3)_3N(OCH_3)I$, with silver benzenesulfinate. These relationships may be expressed in terms of the symbols of positive and negative valence as follows:

$$(CH_3)_3\overset{+}{\equiv}N\overset{-+SO_2C_6H_5}{+-OCH_3} \qquad \text{A}$$

$$(CH_3)_3\overset{+}{\equiv}N\overset{-+OCH_3}{+-SO_2C_6H_5} \qquad \text{B}$$

or according to the more recent theories of Lewis and of Langmuir:



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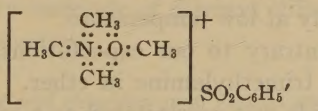

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[1] Vorländer and Nolte, *Ber.*, **46**, 3212 (1913). Kauffmann and Vorländer, *Ber.*, **43**, 2735 (1910).

[2] The yield of chloroplatinate was small, less than 1 g. from 10 g. of trimethylamine.

[3] Jones, *J. Am. Chem. Soc.* **36**, 1268 (1914).

[4] Jones, *Science*, **44**, 493 (1917).

1. Trimethylamine and Benzenesulfonyl Chloride.—It would be natural to expect that a salt as stable as these results of Vorländer and Nolte indicated could be prepared more easily by the direct addition of benzenesulfonyl chloride to trimethylamine. They reported that a "white crystalline mass" was formed when this reaction took place in absolute ether; but, at the same time, they failed to find any of the singular salt in question. They state that the solid appeared to contain the chloride and the benzenesulfonate of trimethylamine.

We have studied the action of benzenesulfonyl chloride upon trimethylamine dissolved in absolute ether. An inspection of the "white crystalline mass" showed that it consisted almost entirely of *tetramethylammonium chloride*. The ether solution, separated from this solid, contained chiefly *benzenesulfone-dimethylamide*. To explain this reaction, formation of an intermediate addition product is assumed, although this seems quite inconsistent in view of the stability of this intermediate salt, as described by Vorländer and Nolte; but no other plausible mechanism suggests itself.

$$(CH_3)_3{\equiv}N\begin{matrix}-SO_2C_6H_5\\-Cl\end{matrix} = (CH_3)_2{=}NSO_2C_6H_5 + CH_3Cl \qquad (2)$$

Methyl chloride acts upon unchanged trimethylamine.

$$(CH_3)_3N + CH_3Cl = (CH_3)_4NCl \qquad (3)$$

The reaction progressed rapidly and smoothly at 0°; and even at the temperature of solid carbon dioxide and ether, although it was somewhat retarded, the same products resulted. We could find no evidence to establish the presence of Vorländer and Nolte's salt.

We also repeated the experiments of Vorländer and Nolte in which water and alcohol solutions of trimethylamine were treated with benzenesulfonyl chloride. From these solutions, chloroplatinates difficultly soluble in water were easily obtained but, after recrystallization from warm water, they gave melting points varying from 215° to 260°. This seemed to indicate a mixture of salts, rather than a homogeneous substance.

2. Trimethylamine and Chlorides of Other Organic Acids.—Toluene-*p*-sulfonyl chloride reacted with trimethylamine less vigorously but essentially in the same manner; tetramethylammonium chloride was formed readily at low temperature.

Contrary to our expectations, benzenesulfinyl chloride failed to react with trimethylamine in ether. A small amount of trimethylammonium chloride was precipitated as a result of some hydrolysis of the very sensitive acid chloride. Some phenyl benzenethiosulfonate, $C_6H_5SO_2.SC_6H_5$, was isolated but this was formed by reactions which did not involve the amine.

Benzoyl chloride in ether at 0°, or in benzene at 80°, showed no tendency to act upon trimethylamine.

Acetyl bromide gave trimethylammonium bromide and ketene. This is

analogous to cases studied by Standinger. On the other hand, Staedel[5] reported that acetyl bromide acted with dimethylaniline to yield methylacetanilide and trimethylphenylammonium bromide, a reaction analogous to that shown by trimethylamine and benzenesulfonyl chloride.[6]

3. Trimethylamine and Nitrosyl Chloride.—If nitrosyl chloride reacted with trimethylamine to form an addition product similar to the one proposed for benzenesulfonyl chloride, and if this dissociated to give methyl chloride, the compounds produced should be dimethylnitrosamine and tetramethylammonium chloride.

$$(CH_3)_3N\overset{-NO}{\underset{-Cl}{}} = (CH_3)_2N{-}NO + CH_3Cl \qquad (4)$$
$$(CH_3)_3N + CH_3Cl = (CH_3)_4NCl$$

Possibly, the dissociation might occur in a different fashion to yield nitrosomethane (or formaldoxime) and dimethylchloro-amine, although this does not seem so plausible.

$$(CH_3)_3N\overset{-NO}{\underset{-Cl}{}} = (CH_3)_2NCl + CH_3NO \qquad (5)$$
$$H_3C{-}NO = H_2C{=}NOH$$

The products actually observed by us were *nitric oxide, trimethylammonium chloride,* accompanied by a substance which appears to be *dimethylchloromethylamine* and by small amounts of *formaldehyde* and *dimethylammonium chloride.* The last two compounds seem to be secondary products and to be caused by the action of moisture. Careful search failed to show the presence of any tetramethylammonium chloride and dimethylnitroso-amine, or of formaldoxime and dimethylchloro-amine.

Briefly, our observations were as follows. When ether solutions of trimethylamine and nitrosyl chloride were mixed, solid products separated at once. At first, this solid assumed an orange color similar to that of nitrosyl chloride, itself, but as the temperature was raised slightly, and while it was still much below 0°, the solid acquired a dark cocoa-brown shade. Almost immediately after this stage was reached, a rapid evolution of gas commenced and the solid became colorless.

The *gas* was shown by quantitative determination to be nitric oxide, free from other oxides of nitrogen; for every molecule of nitrosyl chloride employed, one molecule of nitric oxide was evolved.

[5] Staedel, *Ber.*, **19**, 1947 (1886).

[6] Dehn and his associates studied the action of acid chlorides upon various amines dissolved in ether. With benzenesulfonyl chloride and several tertiary amines, including tripropylamine and triethylamine, they report evidence of the formation of addition products, but the analytical results are not convincing. Pyridine seems to have yielded an actual addition product. [*J. Am. Chem. Soc.*, **34**, 1399 (1912); **36**, 2091 (1914); **39**, 2444 (1917).] Freudenberg and Peters [*Ber.*, **52**, 1463 (1919)] have shown conclusively that addition products of acid chlorides to tertiary amines can be obtained with pyridine and oxalyl chloride or acetyl chloride, if these substances act upon one another in chloroform solution.

The *colorless solid* contained trimethylammonium chloride, a small amount of dimethylammonium chloride, and a substance richer in total chlorine, which appeared to be dimethylchloromethylammonium chloride, $(CH_3)_2(CH_2Cl)\equiv NHCl$. Whenever the solid was exposed to moist air, the odor of formaldehyde became noticeable at once. After contact with moisture for some time, or after treatment with water, only the chlorides of trimethylamine and of dimethylamine accompanied by formaldehyde could be found.

The *ether solution* separated from the solid also contained a substance which gave formaldehyde with water. This appears to be free dimethylchloromethylamine.

Mechanism of the Reaction with Nitrosyl Chloride.—It is difficult to formulate any satisfactory scheme for this reaction. The cocoa-brown solid may be a direct addition product, or it may be some molecular aggregate less definite than this. In any event, the methyl groups of the

$$(CH_3)_3\equiv N + O=N-Cl = (CH_3)_3\equiv N\begin{matrix}-NO\\-Cl\end{matrix} \qquad (6)$$

amine furnish the only source of hydrogen required to produce hydrogen chloride. This would lead to some equation such as the following.

$$(CH_3)_2=N\begin{matrix}-NO\\-Cl\\|\\H_2C-H\end{matrix} = (CH_3)_2=N-NO \begin{matrix}\\\\\|\\H_2C\end{matrix} + HCl \qquad (7)$$

Hydrogen chloride reacts with unchanged amine.

$$(CH_3)_3\equiv N + HCl = (CH_3)_3\equiv NHCl \qquad (8)$$

It is even more difficult to express by an equation the stages which lead to the evolution of nitric oxide equal in amount to the total nitrosyl (NO) radical in the nitrosyl chloride employed. The following equation is proposed.

$$(CH_3)_2=N-NO \begin{matrix}\\\\\|\\CH_2\end{matrix} + O=NCl = (CH_3)_2=N \begin{matrix}\\\\|\\H_2CCl\end{matrix} + 2NO \qquad (9)$$

Some dimethylchloromethylamine, reacting with hydrogen chloride, would be found as a salt in the solid, while some of it would remain dissolved in the ether. Any moisture present during the reaction or introduced while the products are being separated would hydrolyze this amine or its salt.

$$(CH_3)_2=N-CH_2Cl + HOH = (CH_3)_2=NH_2Cl + H_2C=O \qquad (10)$$

It is possible that dimethylchloromethylamine, by intramolecular alkylation and salt formation, may pass to an isomer and that this isomer may

$$(CH_3)_2NCH_2Cl \longrightarrow (CH_3)_2NCl=CH_2 \qquad (11)$$

be responsible for the ease with which hydrolysis occurs; $(CH_3)_3N(CH_2I)I$ appears to yield formaldehyde only with difficulty.

Synthesis of Dimethylchloromethylamine.—It was expected that the chloride of this amine would be formed by the action of methylene chloride upon dimethylamine. During the reaction, about one-half of the dimethyl-

amine was converted into its chloride and deposited as a solid. The liquid portion contained chiefly some unchanged methylene chloride and dimethylamine and considerable tetramethylmethylenediamine. A substance, possibly dimethylchloromethylamine, was present which gave formaldehyde with water. These products suggest the following equations.

$$(CH_3)_2{=}NH + H_2CCl_2 = (CH_3)_2{=}N\overset{H}{\underset{H_2CCl}{\overset{|}{-}Cl}} \qquad (12)$$

Dimethylamine displaced hydrogen chloride from this salt.

$$(CH_3)_2{=}N\overset{H}{\underset{H_2CCl}{\overset{|}{-}Cl}} + (CH_3)_2{=}NH = (CH_3)_2{=}N\underset{H_2CCl}{|} + (CH_3)_2{=}NH_2Cl \qquad (13)$$

Then dimethylchloromethylamine reacted with unchanged dimethylamine to form tetramethylmethylenediamine and hydrogen chloride which, in turn, combined with dimethylamine.

$$(CH_3)_2{=}N{-}CH_2Cl + 2HN(CH_3)_2 = (CH_3)_2N{-}CH_2{-}N(CH_3)_2 + (CH_3)_2{=}NH_2Cl \qquad (14)$$

Houben and Arnold[7] found that diethylchloromethylamine could be obtained in the form of a chloroplatinate from the products of the interaction between diethylamine and methylchloromethyl sulfate.

$$(C_2H_5)_2{=}NH + (CH_3)CH_2Cl.SO_4 = (C_2H_5)_2(CH_2Cl){\equiv}N + CH_3.HSO_4 \qquad (15)$$

The amount of chloroplatinate secured was small but the analysis was satisfactory. They found it necessary to use fresh samples of the chloroplatinate for analysis, since it decomposed very rapidly. When it was crystallized from alcohol, a part of it was changed into diethylammonium chloroplatinate.

Similarly, by the action of methylchloromethyl sulfate upon dimethylamine, we have obtained a chloroplatinate which seems to be a derivative of dimethylchloromethylamine. Recrystallized and dried, it gave positive tests for formaldehyde by the usual methods.

Experimental Part

I. Action of Trimethylamine upon Benzenesulfonyl Chloride

Trimethylammonium chloride was prepared from trioxymethylene and ammonium chloride.[8]

A solution of 9.2 g. of trimethylamine in 50 g. of absolute ether was placed in a small flask attached to a reflux condenser and, after it had been cooled to 0°, 13.7 g. of benzenesulfonyl chloride was added to it slowly through the top of the condenser. A white precipitate appeared almost immediately and considerable heat was evolved. The mixture was allowed to stand undisturbed for a short time. The precipitate (7.5 g.) was collected on a filter, washed quickly with ether and dried in a desiccator. It was recrystallized by dissolving it in alcohol and precipitating it with ether. This salt

[7] Houben and Arnold, *Ber.*, **41**, 1568 (1908).

[8] Adams, "Organic Syntheses," John Wiley and Sons, New York, **1921**, Vol. I, pp. 75, 79.

volatilized when heated to 300–315°, and gave a chloroplatinate difficultly soluble in water which melted with decomposition at 290–295°. Upon analysis it was found to contain a small amount of sulfur as an impurity, but this was removed by recrystallizing it from alcohol and ether.

Anal. Subs., 0.3374: AgCl, 0.4326. Calcd. for $(CH_3)_4NCl$: Cl, 32.39. Found: 31.72.

The insolubility of the solid in chloroform established the absence of dimethylammonium and of trimethylammonium chlorides, which are readily dissolved by this solvent. A negative carbylamine test with alcoholic potassium hydroxide and chloroform showed the absence of monomethylamine salt. These results, together with the analysis, prove the white salt to be tetramethylammonium chloride.

The filtrate and the ether washings were combined, evaporated as far as possible at room temperature, and the oily residue was distilled under reduced pressure. Two fractions were collected: the first consisted of a small amount of unchanged acid chloride; the second was dissolved in benzene and petroleum ether and, after partial evaporation of the solvents, gave white, needle-like crystals of benzenesulfone-dimethylamide; m. p., 47–48°. Hydrolysis of the entire amount of sulfonamide with dil. sulfuric acid, followed by distillation of the solution made alkaline with sodium hydroxide, set free dimethylamine which was absorbed in hydrochloric acid; the acid solution, evaporated to dryness, gave 3.6 g. of the hydrochloride; m. p., 171°.

The following equations express the course of the reaction.

$$(CH_3)_3N + C_6H_5SO_2Cl = CH_3Cl + (CH_3)_2N.SO_2.C_6H_5 \qquad (16)$$
$$(CH_3)_3N + CH_3Cl = (CH_3)_4NCl$$

Even when the experiment was carried out at the temperature of a mixture of carbon dioxide snow and ether, no traces of the desired addition product could be obtained. The reaction took place much more slowly; tetramethylammonium chloride was precipitated and benzenesulfone-dimethylamide was found in the ether filtrate.

Repetition of Vorländer and Nolte's Experiments.—1. Benzenesulfonyl chloride was added slowly and in slight excess to a 10% solution of trimethylamine in water. (About 16 g. of acid chloride was required for 100 cc. of 10% trimethylamine solution.) After a short time the reaction mixture was shaken with ether to remove the excess of benzenesulfonyl chloride. Chloroplatinic acid was added to the solution and orange-colored crystals were obtained. The melting points were very indefinite, even after fractional recrystallization of the crystals from hot water; they ranged from 215° to 260°.

2. To 10 cc. of aqueous 33% trimethylamine solution 18 cc. of alcohol and 3 cc. of water were added to give approximately a 10% solution. The mixture was cooled to 10° and 6 g. of benzenesulfonyl chloride was added very slowly. The small layer of oily ester was separated and the turbid solution cleared by filtration. When chloroplatinic acid was added to a small amount of this liquid a chloroplatinate separated at once. This, after recrystallization from warm water, gave crystals melting from 255–262°. A very small amount of the chloroplatinate difficultly soluble in warm water melted from 215–225°. Part of the aqueous alcoholic solution was evaporated to about one-fourth its original volume, and a very small amount of white crystals separated when the solution was cooled. Silver nitrate solution precipitated no chloride from a warm aqueous solution of these crystals. Possibly they were trimethylammonium benzenesulfonate.

Anal. Subs., 0.3188: $BaSO_4$, 0.3390. Calcd. for $(CH_3)_3NH.OSO_2C_6H_5$: S, 14.74. Found: 14.64.

II. The Action of Trimethylamine upon Nitrosyl Chloride

Nitrosyl chloride, prepared by heating nitrosylsulfuric acid with dry

sodium chloride, was passed over calcium chloride and then liquefied in a spiral condenser surrounded by a freezing mixture of salt and ice.

For analysis, a small bulb containing a weighed sample of substance was broken by shaking it with 100 cc. of a 1% solution of potassium hydroxide in a small bottle. The solution was washed into a beaker, filtered, the filtrate acidified with dil. nitric acid and the chloride precipitated with silver nitrate.

Anal. Subs., 0.1075, 0.0394: AgCl, 0.2305, 0.0854. Calcd. for NOCl: Cl, 54.16. Found: 53.05, 53.60.

Trimethylamine was prepared as described earlier in this paper. Traces of formaldehyde were found in the chloride, so the salt was dissolved in chloroform and precipitated by ether until formaldehyde was removed completely.

A solution of 20 g. of dry trimethylamine in 75 cc. of absolute ether was placed in a flask connected with a reflux condenser and cooled in carbon dioxide snow and ether. Then 20 g. of nitrosyl chloride, dissolved in 50 cc. of previously cooled ether, was run into this solution slowly through a dropping funnel. Even at this low temperature the reaction began in a few minutes and an orange-colored solid material formed. When the temperature was raised very gradually, this product became cocoa-brown in color and, at this stage, the evolution of a colorless gas started almost immediately. Within the course of a few minutes (depending upon the temperature, which still was kept below zero) the brown color of the solid had entirely disappeared and a white granular substance remained suspended in the ether. The flask was warmed slightly to remove the gas as completely as possible. The solid (29 g.) was removed to a filter, washed quickly with ether and dried in a desiccator.

A. Inspection of the Gas.—The gas was colorless but immediately became brown when it was exposed to air. Several experiments were performed with 1 g. of trimethylamine and one equivalent of nitrosyl chloride. The air was partially displaced from the system by ether vapor. Samples of the gas showed only a very slight absorption in the presence of a 50% solution of potassium hydroxide, which led us to believe that nitrogen dioxide or nitrogen trioxide was not formed in the reaction, and that the observed absorption was to be explained by the union of nitric oxide with some oxygen present in the system. With a 33% solution of ferrous sulfate there was absorption of the gas amounting to 60–70%. Subsequently, alcohol absorbed none of the residual gas, showing that probably no nitrous oxide was present. The residual gas appeared to be nitrogen which was present in the apparatus at the beginning of the experiment. Thus, our results showed that the gas was nitric oxide.

Anal. Gas taken, 99.9 cc.: absorbed by KOH, 4.7 cc.; absorbed by $FeSO_4$, 67.7 cc.; absorbed by alcohol, none; residue (N_2), 27.5 cc.

We then determined quantitatively the amount of nitric oxide which was evolved during the reaction between 0.9 g. of trimethylamine and 1 g. (one equivalent) of nitrosyl chloride. After air had been removed from the system by a stream of dry nitrogen, the reactants were added, and the gas was displaced by a stream of nitrogen. It was passed through a small glass spiral surrounded by a freezing mixture of carbon dioxide snow and ether to condense any volatile matter such as ether, nitrosyl chloride or amine. It was then absorbed by an acidified solution of potassium permanganate in a Friedrichs spiral gas-washing bottle. Excess of a standard solution of ferrous ammonium sulfate was added and the excess titrated with permanganate. The results obtained showed that the amount of nitric oxide evolved was equivalent to the nitrosyl chloride used in the reaction.

Anal. 100 cc. of 0.5 *N* $KMnO_4$ used to absorb NO (50 cc. of 2 *N* H_2SO_4 per 100 cc. of $KMnO_4$), 49.1 cc. of 0.1 *N* $FeSO_4.(NH_4)_2SO_4.6H_2O$ added; 0.2 cc. of $KMnO_4$ required

to neutralize the excess of $FeSO_4.(NH_4)_2SO_4$; $10NO + 6KMnO_4 + 9H_2SO_4 = 3K_2SO_4 + 6MnSO_4 + 10HNO + 4H_2O$; 1.428 g. of $KMnO_4$ required to oxidize the NO = 0.45 g. of NO. Calcd.: NO from 1 g. of NOCl = 0.46 g.

The gas not acted upon by permanganate was tested with ferrous sulfate but no absorption took place, so all of the nitric oxide must have reacted with the permanganate.

B. Inspection of the Solid.—An intense odor of formaldehyde was observed both with the crystals and with the ether filtrate. Even after the solid was thoroughly dry, formaldehyde could be detected whenever it was exposed to moist air. The crystals were found to be completely soluble in cold chloroform, which established the absence of any tetramethylammonium chloride.

Some of the original white solid was recrystallized by dissolving it in cold alcohol and reprecipitating it with ether. During this operation, an intense odor of formaldehyde was noticed. The amines liberated from 3.9 g. of this purified salt by heating it with a solution of potassium hydroxide were collected in hydrochloric acid and the solution was evaporated to dryness. The residue was dissolved in a small amount of water, the solution cooled to 0° and treated with excess (4 molecular equivalents) of a 12% solution of potassium hydroxide and 1.5 equivalents of benzenesulfonyl chloride. The solid product that separated at once was collected and recrystallized from ether; weight, 3 g.; m. p., 45–46°. It was, therefore, benzenesulfone-dimethylamide, which established the presence of dimethylammonium chloride or, possibly, of dimethylchloromethylammonium chloride, in the original product.

The alkaline filtrate was distilled in a current of steam, the distillate collected in hydrochloric acid, and the solution evaporated to dryness on a water-bath. The residue (1.5 g.) consisted of trimethylammonium chloride; it melted at 270–271°, and formed a chloroplatinate that melted at 241–243°.

When the amines were liberated from another portion of the original salt and a solution of *p*-nitrophenylhydrazine in acetic acid was added, a flocculent, yellow precipitate appeared in the course of a few minutes; this was formaldehyde *p*-nitrophenylhydrazone; m. p., 180–181°.

C. Inspection of the Ether Filtrate.—When the filtrate originally separated from the solid was distilled, a very small amount (1 cc.) of brown oil remained. This solidified partially; the solid melted between 50° and 60°. The amount of crystals obtained was too small to work with further, but they appeared to consist of a polymer of formaldehyde. They gave tests for formaldehyde.

If dimethyl nitrosamine had been formed as one of the products (see Equations 4 and 5 on p. 5), it would have been obtained by removal of the ether from the original filtrate. This nitrosamine is a yellow oil that boils at 153° (774 mm.). It is decomposed when heated with hydrochloric acid to give dimethylamine and nitrous acid, but we could not identify either of these products when the brown oil obtained by evaporation of the ether was heated with concd. hydrochloric acid. Furthermore, neither dimethylchloro-amine nor formaldoxime was formed in the reaction. Both of these products would have been held in the ether solution and would have been easily detected. The chloro-amine is a pungent-smelling liquid which boils at 46° and the formaldoxime is a colorless liquid boiling at 84° which gradually gelatinizes at ordinary temperature because of polymerization.

III. Action of Dimethylamine with Methylene Iodide and with Methylene Chloride

It seemed desirable to prepare dimethylchloromethylamine for purposes of identification in connection with this reaction. The following experiments were undertaken with this object in view.

Dimethylamine and Methylene Iodide.—A solution of 1.5 g. of dimethylamine in 15 cc. of absolute ether was treated at room temperature with 9 g. of methylene iodide. A stream of dry air was passed through the reaction flask. After a short time an oily layer separated and, upon shaking the flask, this gradually solidified. The solid was collected on a filter, washed with ether in an atmosphere of dry air and removed quickly to a desiccator. The analysis showed that it was dimethylammonium iodide.

Anal. Subs., 0.3010: AgI, 0.4103. Calcd. for $(CH_3)_2NH_2I$: I, 73.81. Found: 73.68.

The ether filtrate was distilled to remove the solvent. The residue was a colorless, mobile liquid smelling strongly of formaldehyde. Probably it was chiefly tetramethylmethylenediamine. (See experiments under methylene chloride.)

When dimethylamine and methylene iodide were allowed to react in the absence of a solvent, sudden decomposition often took place, even at comparatively low temperatures. The reaction seemed to proceed quietly for several minutes and small white crystals were deposited. Suddenly a reaction started with explosive violence. The mixture became dark brown, an intense odor of formaldehyde was noticed in the cloud of violet vapors which escaped and dimethylammonium iodide and free iodine were formed. Several experiments of this nature were made, but the reaction proceeded quietly in only one instance; dimethylammonium iodide was deposited. In absolute alcohol, the reaction took place smoothly to form dimethylammonium iodide as the only crystalline product.

Dimethylamine and Methylene Chloride.—A solution of 10 g. of dimethylamine in 18.8 g. of methylene chloride was heated to 70° in a sealed tube immersed in a water-bath. At 60–70° the liquid became slightly greenish in color and, almost immediately, a mass of white crystals separated.

After keeping the tube at this temperature for three hours, it was opened and the liquid portion distilled directly from the tube, while a current of dry nitrogen gas was passed through the system. The crystalline residue which remained in the tube was dimethylammonium chloride (m. p., 171°) which was analyzed immediately. Weight, 8 g.; so approximately one-half of the dimethylamine present was converted into its chloride.

Anal. Subs., 0.1659: AgCl, 0.2907. Calcd. for $(CH_3)_2NH_2Cl$: Cl, 43.55. Found: 43.35.

The liquid was fractionated very carefully and resolved into two main fractions: one fraction boiled between 40–50° and was chiefly unchanged methylene chloride; the other distilled between 75° and 85° and had a very sharp, penetrating odor. After exposure to air or treatment with water, formaldehyde could be detected in each fraction.

The second fraction possessed the properties of tetramethylmethylenediamine, $(CH_3)_2N{-}CH_2{-}N(CH_3)_2$, described by Henry, who prepared it by allowing formaldehyde and dimethylamine to react in cold aqueous solution. Henry[9] found that his substance was hydrolyzed by hydrochloric acid to give formaldehyde and dimethylammonium chloride, and this is also the case with the products obtained in the reactions between dimethylamine and methylene chloride. These results showed that it was impractical to prepare a salt of dimethylchloromethylamine by these reactions. The following experiments were performed with the hope of securing it.

IV. The Action of Methylchloromethyl Sulfate upon Dimethylamine

Twenty-five g. of chlorodimethyl ether[10] was cooled to 0°, and sulfur trioxide (obtained by gently heating 50% fuming sulfuric acid) passed into it until an increase in

[9] Henry, *Bull. Acad. roy. Belgique,* [3] **26,** 203; **28,** 368; *Ber.*, **26,** Ref., 934 (1893); *Ber.*, **28,** Ref., 852 (1895).

[10] Houben and Arnold, *Ber.*, **40,** 4308 (1907).

weight of 25 g. had taken place. The brownish, oily liquid was then distilled several times at 18 mm. pressure. The fraction that boiled between 90° and 92° was finally collected. It was a heavy, oily liquid, almost colorless.

A solution of 7 g. of this methylchloromethyl sulfate (2 molecular equivalents) in 50 cc. of absolute ether was cooled in a flask attached to a reflux condenser by surrounding it with a freezing mixture of carbon dioxide snow and ether. Then 1 g. of dimethylamine in 10 cc. of ether was added slowly through the top of the condenser, which was protected from moisture by a calcium chloride tube. A white, semi-solid product separated at once. After five minutes the ether was decanted, and a stream of dry air was passed through the flask to remove as much of the ether as possible. The solid residue was very hygroscopic and gave distinct tests for formaldehyde and dimethylamine. A concentrated alcoholic solution of chloroplatinic acid added to a portion of it gave an orange chloroplatinate, soluble in water, but insoluble in alcohol. The chloroplatinate gave positive tests for formaldehyde when tested by Leache's method or when treated with resorcinol and sulfuric acid. It was hygroscopic, and had no sharply-defined melting point.

Anal. Subs., 0.0754: Pt, 0.0230. Calcd. for $C_6H_{18}Cl_8N_2Pt$: Pt, 32.68. Found: 30.50.

Any trimethylammonium chloride which might have been formed by the action of the sulfate upon dimethylamine would have given a chloroplatinate soluble in alcohol.

Summary

1. Vorländer and Nolte have described a quaternary ammonium salt, formed by the addition of benzenesulfonyl chloride to trimethylamine. Their experiments were repeated, but it was found that even in absolute ether at very low temperatures this salt could not be isolated; the products were tetramethylammonium chloride and benzenesulfone-dimethylamide. Toluenesulfonyl chloride and trimethylamine react in a similar way.

2. The action of several other organic acid chlorides upon trimethylamine has been studied, namely, benzenesulfinyl chloride, acetyl bromide and benzoyl chloride.

3. When nitrosyl chloride and trimethylamine react at low temperatures the products observed are nitric oxide, trimethylammonium chloride, probably dimethylchloromethylamine, and small amounts of formaldehyde and dimethylammonium chloride. A scheme has been proposed to explain the mechanism of this reaction.

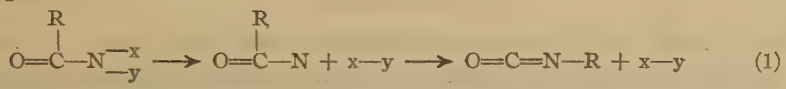
Dimethylamine and methylene chloride do not react to form dimethylchloromethylammonium chloride. The products are tetramethylmethylenediamine and dimethylammonium chloride. Probably dimethylchloromethylamine is formed in an intermediate stage of the reaction. The reaction of methylene iodide with dimethylamine is more complicated.

Experiments were made to prepare dimethylchloromethylamine by the action of methylchloromethyl sulfate upon dimethylamine. An unstable chloroplatinate was obtained which appears to be the chloroplatinate of this amine.

THE ACTION OF HYDROXYLAMINE UPON SULFINIC ACIDS AND THEIR DERIVATIVES

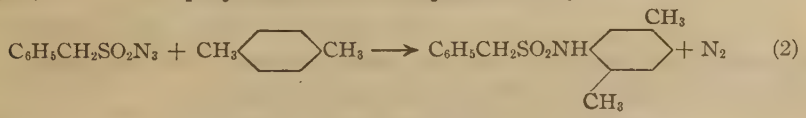
Introduction

Many organic derivatives of nitrogen, such as hydroxamic acids, halogen amides, azides and other similar compounds, are particularly sensitive to changes which involve molecular rearrangements. In all such cases, some radical attached to a carbon atom "wanders" to a nitrogen atom; the first tangible product of rearrangement observed is an isocyanate. Stieglitz[1] was the first to propose a satisfactory theory which correlates all rearrangements of this type; he assumed the formation of an intermediate product, a derivative of univalent nitrogen, to be the prime essential to such rearrangements.



(1)

But there are certain organic acids which yield derivatives of the favorable type mentioned above, and yet these derivatives show no inclination to undergo rearrangement. Thus, several investigators[2] have failed to find evidence of rearrangement in the case of halogen derivatives of benzenesulfonamide, $C_6H_5SO_2NHX$, although such compounds might be expected to resemble halogen amides of carboxylic acids in this particular. Furthermore, Curtius and Hass[3] observed a similar indifference on the part of the azide of benzenesulfonic acid, $C_6H_5SO_2N_3$. In this instance, the failure to rearrange cannot be attributed to the inability of the group N_3 to lose nitrogen (N_2), because even hydrocarbons such as toluene react with this azide. Similarly, the azide of benzylsulfonic acid, $C_6H_5CH_2SO_2N_3$, reacts with *p*-xylene and with naphthalene by addition.



(2)

The observations made by Piloty[4] in the study of benzenesulfonhydroxamic acid show that this acid departs radically from the usual reaction ex-

[1] Stieglitz, *Am. Chem. J.*, **18**, 751 (1896); **29**, 49 (1903).

[2] Hoogewerff and van Dorp, *Rec. trav. chim.*, **6**, 373 (1888); *Ber.* (Ref.) **21**, 291 (1888). Chattaway, *J. Chem. Soc.*, **87**, 145 (1905).

[3] Curtius and Hass, *J. prakt. Chem.*, **102**, 87 (1921).

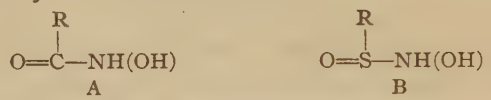
[4] Piloty, *Ber.*, **29**, 1560, 2324 (1896).

pected of a monohydroxamic acid; no rearrangement has been observed. Concentrated solutions of alkalies cause a decomposition of it in the following way.

$$2C_6H_5SO_2NHOH + 4KOH \longrightarrow 2C_6H_5SO_2K + K_2N_2O_2 + 4H_2O \qquad (3)$$

A sulfinate and a hyponitrite are formed.

The departure from the norm displayed by these derivatives of sulfonic acids suggested the problem of preparing derivatives of benzenesulfinic acid. From a theoretical point of view this would be quite alluring, for the hydroxamic acids (azides, or halogen amides) of benzenesulfinic acid and of carboxylic acids are similarly constituted, and might be expected to show a similarity in chemical behavior.



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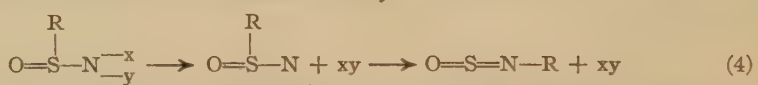
Furthermore, the thionylamines which would be expected as the rearrangement products of a sulfinhydroxamic acid or its derivatives, are known compounds and could be identified easily.



(4)

We have tried to prepare the hydroxamic acids of benzenesulfinic acid and of *p*-toluenesulfinic acid. Most of the methods commonly employed in making hydroxamic acids of carboxylic acids were applied; the action of free hydroxylamine upon the acid chlorides, the amides or esters, and the thermal decomposition of the hydroxylammonium salt. Ethyl benzenesulfinate showed no tendency to react with free hydroxylamine; in the other cases, even when the reaction was carried out in absolute ether at the temperature of solid carbon dioxide and ether, the chief product observed was *benzenesulfonamide, $C_6H_5SO_2NH_2$, not benzenesulfinhydroxamic acid.*

There are at least two ways of explaining these results. In the first place, benzenesulfinhydroxamic acid may be formed, and then converted into the amide by indirect oxidation.

$$C_6H_5SO{-}NH(OH) \longrightarrow C_6H_5SO_2NH_2 \qquad (5)$$

In the second place, hydroxylamine might act upon the derivative of benzenesulfinic acid directly as an oxidizing agent. With benzenesulfinyl chloride the reaction would be formulated as follows:

$$\begin{aligned} NH_2OH + C_6H_5SOCl &\longrightarrow NH_3 + C_6H_5SO_2Cl \\ C_6H_5SO_2Cl + 2NH_3 &\longrightarrow C_6H_5SO_2NH_2 + NH_4Cl \end{aligned} \qquad (6)$$

If the second interpretation were correct, it would be expected that benzenesulfonyl chloride would convert some of the hydroxylamine into benzenesulfonhydroxamic acid (Piloty's acid), $C_6H_5SO_2NHOH$, which is a solid, melting at about 126°; but no trace of this acid could be found among the products. Therefore, the first interpretation appears more plausible.

Furthermore, benzenesulfinic acid, itself, reacts smoothly with free hydroxylamine to give a salt:

$$C_6H_5SO.OH + NH_2OH \longrightarrow C_6H_5SO.ONH_3(OH) \qquad (7)$$

No oxidation of the sulfinic acid was observed in the preparation of this salt since the product contained no ammonium benzenesulfonate. When it was heated it lost water. By this change we hoped to secure benzenesulfinhydroxamic acid, just as certain hydroxylammonium salts of carboxylic acids yield hydroxamic acids.[5]

$$\begin{matrix} RCO.ONH_3(OH) \longrightarrow RCO.NH(OH) + H_2O \\ RSO.ONH_3(OH) \longrightarrow RSO.NHOH + H_2O \end{matrix} \qquad (8)$$

But in this case, also, only benzenesulfonamide was isolated.

Some of these experiments were repeated with *p*-toluenesulfinic acid. In these reactions no evidence of the hydroxamic acid was secured. The amide of *p*-toluenesulfonic acid was the chief reaction product.

Experimental Part

I. Action of Hydroxylamine upon Benzenesulfinic Acid and Its Derivatives

Benzenesulfinic acid was prepared according to the Friedel-Crafts method[6] by passing dry hydrogen chloride and sulfur dioxide into benzene in the presence of aluminum chloride.

Hilditch and Smiles[7] state that benzenesulfinyl chloride may be prepared as a solid (m. p., 38°) by the action of thionyl chloride upon benzenesulfinic acid in petroleum ether. Their work was repeated, but no acid chloride could be obtained. The oil that remained after evaporation of the petroleum ether gave a small amount of a brownish solid when ether was added to it. These crystals melted at 42–44°, were insoluble in water or in a solution of potassium hydroxide, and consisted of the phenyl benzenethiosulfonate, $C_6H_5SO_2.S.C_6H_5$. When the ether filtrate was evaporated, crystals of benzenesulfinic acid remained.

According to Braun and Kaiser,[8] benzenesulfinyl chloride can be prepared as a liquid by distillation of the product obtained by the action of benzenesulfinic acid and thionyl chloride.

Twenty-five g. of benzenesulfinic acid was treated, at 0°, with 25 g. of thionyl chloride and, after the reaction had ceased, the flask was warmed slightly on the water-bath. The excess of thionyl chloride[9] was removed in a vacuum, first at room tem-

[5] Jones and Oesper, *Am. Chem. J.*, **42**, 518 (1909).

[6] Knoevenagel and Kenner, *Ber.*, **41**, 3315 (1908).

[7] Hilditch and Smiles, *Ber.*, **41**, 4113 (1908).

[8] Braun and Kaiser, *Ber.*, **56B**, 549 (1923).

[9] The thionyl chloride was purified and the yellow color entirely removed by distillation, first over quinoline, then over linseed oil and finally over pure beeswax. The chloride purified in this manner apparently contains no impurities which may act cata-

perature, and finally at 50°. The oil that remained was distilled at a pressure of 3–4 mm.; it boiled at 85–90°. It was a light yellow liquid that fumed in the air, and was very readily hydrolyzed to yield benzenesulfinic acid.

A. Action of Hydroxylamine upon Benzenesulfinyl Chloride

1.—A solution of 5.6 g. of benzenesulfinyl chloride in 15 cc. of absolute ether was treated, at 0°, or at the temperature obtained by solid carbon dioxide and ether, with 2.3 g. (two equivalents) of free hydroxylamine. The hydroxylamine was added very slowly while the solution was shaken. A white crystalline product was removed to a filter, washed quickly with ether, and dried in a desiccator. The dry substance was extracted with benzene; the portion of the solid (1.8 g.) which was insoluble in the benzene melted at 84–85°. It showed the characteristic behavior of an hydroxylamine salt, and consisted of basic hydroxylammonium chloride, $(NH_2OH)_2.HCl$, which melts at 85°. The benzene solution was evaporated, and a small crystalline residue obtained which melted between 136° and 145°. When it was recrystallized from warm water, colorless plates, m. p. 150–151°, separated. The ether filtrate and washings were evaporated to dryness on the water-bath. The residue melted at 145–150° and weighed 4.2 g. Recrystallized from warm water, it melted at 150°. Its properties corresponded with those of benzenesulfonamide.

No test for an hydroxamic acid could be obtained.

Anal. Subs., 0.2250: $BaSO_4$, 0.2758. Calcd. for $C_6H_7SO_2N$: S, 20.37. Found: 19.84.

2.—A solution of 2.1 g. of sodium hydroxide in a small amount of water was added to a concentrated solution of 1.8 g. of hydroxyl-ammonium chloride in water. Then 4.2 g. of benzenesulfinyl chloride was added slowly. The solid which formed was separated, dried and extracted with ethyl acetate. The insoluble residue, crystallized from water, gave white crystals that melted at 150–151° (3.5 g.).

Anal. Subs., 0.1732: $BaSO_4$, 0.2565. Calcd. for $C_6H_5SO_2.NH_2$. S, 20.37. Found: 20.33.

It did not reduce ammoniacal silver nitrate. This excluded the possibility of the presence of any hydroxamic acid. In fact, the white silver salt of benzenesulfonamide was obtained by adding silver nitrate to a slightly ammoniacal solution of it.

B. Hydroxylammonium Salt of Benzenesulfinic Acid.—Free hydroxylamine was added to a cold alcohol solution of the acid, and the salt was precipitated by ether. Recrystallized from methyl alcohol and ether it gave colorless crystals that melted at 83–85°.

Anal. Subs., 0.1975: N_2, 13.1 cc. Calcd. for $C_6H_5SO.ONH_3OH$: N, 8.00. Found: 7.81.

A sample of the salt weighing 1.98 g. was heated for ten hours at 100–110° in an oil-bath. The tube containing the salt was attached to a weighed calcium chloride tube. When the weight of the sample had become constant, the increase in weight of the calcium chloride tube amounted to 0.1550 g. (calculated, 0.23 g.). The residue in the tube was extracted with ether and, after evaporation of the solvent and recrystallization of the brownish residue from warm water, white crystals were obtained, which melted at 150° and had the characteristic properties of benzenesulfonamide.

C. Action of Hydroxylamine upon Benzenesulfinamide.—Equivalent amounts of this amide and of hydroxylammonium chloride were dissolved in water and alcohol and the solution was allowed to stand for 15 hours at room temperature.

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lytically. [Hans Meyer and Schlegl, *Monatsh.*, **34**, 569 (1913).] Hans Meyer, "Analyse und Konstitutionsermittlung Organischer Verbindunge," [J. Springer, Berlin, **1916**, third ed., p. 556].

In a second experiment, benzenesulfinamide in absolute alcohol was treated with one equivalent of free hydroxylamine. The temperature of the mixture was maintained at the boiling point for 24 hours. Solids were obtained from these reaction mixtures which, after recrystallization from water, yielded crystals of benzenesulfonamide; m. p., 150–151°.

II. Action of Hydroxylamine upon *p*-Toluenesulfinyl Chloride

p-Toluenesulfinic acid was made by the method suggested by Knoevenagel and Kenner[6] and from it *p*-toluenesulfinyl chloride was prepared by the method of Braun and Kaiser.[8]

1.—A solution of 8.4 g. of hydroxylammonium chloride in 32 cc. of water containing 9.6 g. of sodium hydroxide was treated with 3.5 g. of toluenesulfinyl chloride. The reaction product, a white crystalline material weighing 3.1 g., was extracted with ether, and after evaporation of the solvent, the residue was recrystallized from water, forming white crystals; m. p., 136°. No test for a hydroxamic acid could be obtained. The crystals consisted of *p*-toluenesulfonamide.

Toluenesulfinyl chloride was dissolved in dry benzene and the solution treated with free hydroxylamine. The observations were similar to those recorded for benzenesulfinyl chloride. Crystals of *p*-toluenesulfonamide, m. p. 135–136°, were obtained but no hydroxamic acid.

Summary

The hydroxamic acids of sulfinic acids possess a constitution similar to that of the hydroxamic acids of carboxylic acid. Consequently, they would be expected to show a similar chemical behavior, undergoing rearrangement to form thionylamines, which are well known and easily identified.

However, all attempts to prepare the hydroxamic acids of benzenesulfinic and *p*-toluenesulfinic acids, even when the reactions were carried out in absolute ether at low temperature, resulted in the formation of the corresponding sulfonamides.

The most plausible explanation of these results assumes the formation of the hydroxamic acid, followed by immediate intramolecular oxidation to give benzenesulfonamide.

The hydroxylammonium salt of benzenesulfinic acid, $C_6H_5SO_2NH_3(OH)$, was prepared. When it was heated, water was eliminated, but benzenesulfonamide and not benzenesulfinhydroxamic acid was formed.

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